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ABSTRACT

Five elements are identified as being potentially hazardous in this module. These are boron, cadmium, copper, molybdenum, and nickel. The hazards to plants and animals posed by these elements are discussed in some detail. The sources of toxic elements in sewage and the factors that effect the uptake of toxic elements by sewage sludge are also discussed. Methods of computing allowable sludge loading rates to land are discussed and compared. Sludge loading on the basis of potentially toxic elements is compared to the nitrogen basis and the specific limitations which cadmium may exert. (BB)

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Land Application of Wastes

An Educational Program

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Ithaca, New York

POTENTIALLY TOXIC ELEMENTS

Module 11

January, 1978

SE 025 025

LAND APPLICATION
OF WASTES -
AN EDUCATIONAL PROGRAM

The objective of this program is to increase the knowledge of engineers, scientists, waste management specialists and other practitioners in the concepts and principles needed to properly utilize the potential of land for the application of wastes. It is designed for individuals concerned with waste disposal alternatives for municipal, industrial, and agricultural wastes. The modules in this Program incorporate knowledge from sanitary and environmental engineering, agronomy, soil science, agricultural engineering, economics, and law.

The program consists of some twenty-five modules and audio-visual materials as appropriate.

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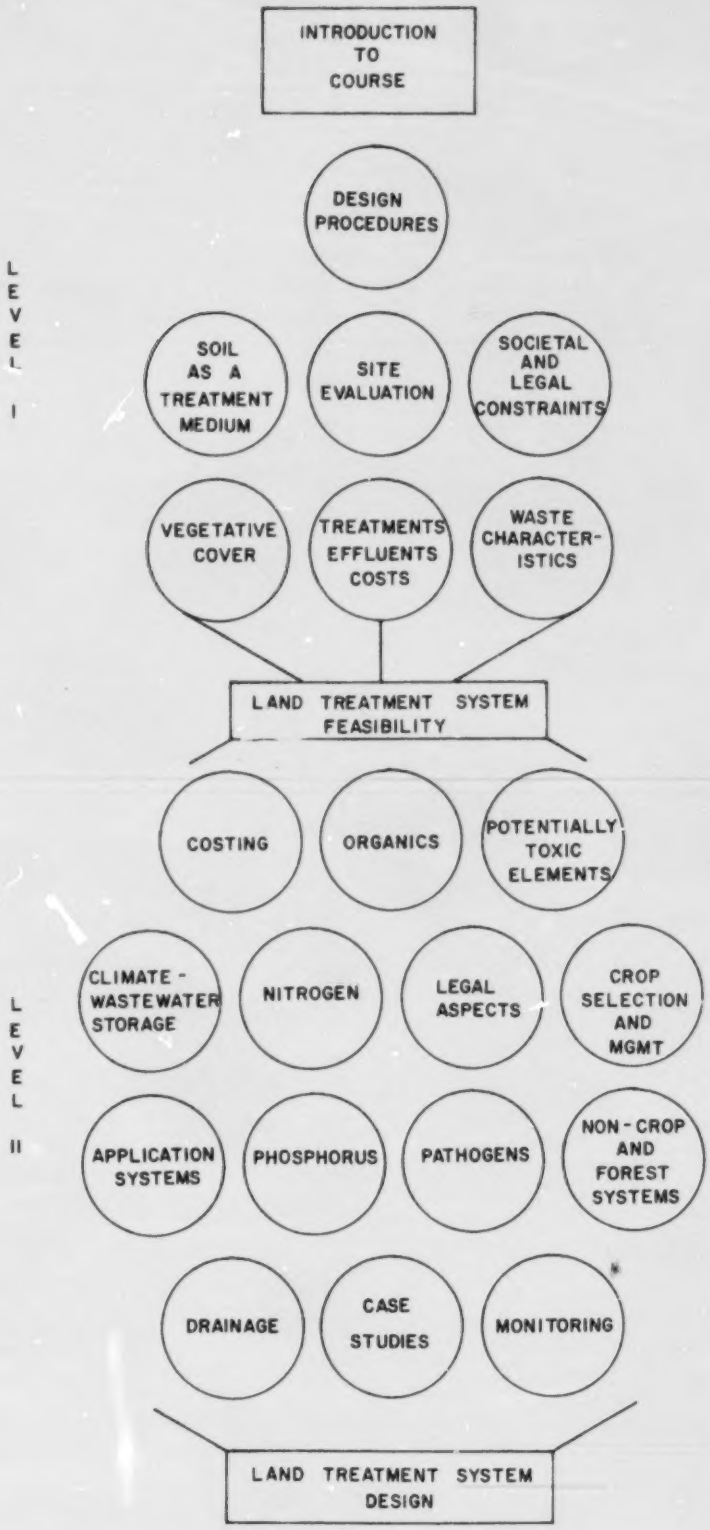

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Summary

Potentially toxic elements enter sewages from residential, urban environmental, and industrial sources. The major portion of toxic element loads carried by sewages is transferred to sludges in conventional primary and secondary wastewater treatment. Secondary effluents generally contain less potentially toxic element concentrations than maximum permissible levels set by the EPA for drinking or irrigation waters. Dissolved salts and nitrogen in effluents can produce toxic conditions.

When sludges are applied to soils, toxic elements interact with both the organic and inorganic matter of soil. Chemical reactions also occur within the soil pore space. The net result is that toxic elements may become available to vegetation and to the animals consuming that vegetation. It is at this point that the toxic potential of these elements may be realized. The effect can be manifested as reduced crop yields, as diminished vegetative cover, or as sickly animals.

Certain crops exhibit varying response to potentially toxic elements. Brief mention of crop responses is made in this module. Hazards to plants and animals posed by selected elements is discussed in some detail. Five elements are catagorized as exerting potentially serious effects: B, Cd, Cu, Mo, and Ni. The toxic effects of boron and nickel are most important in terms of their phyto-toxicity - or toxicity to plants - rather than detrimental effects on animals and humans.

Methods of computing allowable sludge loading rates to land are discussed and compared. Sludge loading on the basis of potentially toxic elements is compared to the nitrogen basis and the specific limitations which cadmium may exert.

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Glossary

cation exchange capacity (CEC) - A measure of the ability of the soil to retain positively charged ions (cations). Generally serves as a rough index of all reactions occurring between charged species and colloidal surfaces. CEC is a function of both the relative intensity of attraction between ions and soil surfaces and the relative concentration of exchangeable ions present in the soil solution.

chelate - A molecular structure in which a heterocyclic ring can be formed by the unshared electrons of neighboring atoms.

electrostatic bond - A chemical bond in which two atoms are kept together by forces caused by transferring one or more electrons from one atom to the other.

heavy metal - A metal whose specific gravity is approximately 5.0 or greater.

ligand - The molecule, ion, or group bound to the central atom in a chelate or a coordination compound. Example: the ammonia molecules in $[Co(NH_3)_6]^{+3}$.

methylation - Formation of an organic compound in which the hydrogen of the hydroxyl group (OH^-) of methyl alcohol is replaced by a metal.

phytotoxic - Poisonous to plants.

precipitation - The production of a solid or solid phase chemically separated from a solution.

reversion - Immobilization of ions by substitution in the crystal lattice of soil solids.

solubility product constant (K_{sp}) - A constant expressed as the product of the molar concentrations of ions in equilibrium with their electrolyte, or combined form.

toxic - Harmful, destructive or deadly; poisonous.

zinc equivalent (ZE) - A coefficient expressing the concentration of zinc, copper, and nickel, assuming copper to be two times as toxic and nickel eight times as toxic as zinc. Thus: $ZE = [Zn^{+2}] + 2[Cu^{+2}] + 8[Ni^{+2}]$, usually expressed in µg/gm.

Objectives

Upon completion of this module, the participant should be able to:

1. Name five elements considered to pose a potentially serious hazard in land application systems. Indicate which are phytotoxic.

2. Describe the general types of crops which are most susceptible and least susceptible to damage from potentially toxic elements.

3. Generally relate the various contributors of potentially toxic elements to municipal sewage.

4. Compare the various approaches to calculating permissible sludge application rates. Indicate the strengths and weaknesses of each approach.

Introduction: Potentially Toxic Elements and their Sources

Identification of Toxic Elements:

The elements listed as potentially toxic vary somewhat with authors, although the inconsistencies are comparatively minor. The toxic elements identified in Table 1 are those included in the lists of maximum contaminant levels in drinking water (Train, 1975) and irrigation water (EPA, 1975b) set by the Environmental Protection Agency. Most of these elements, along with a few others, are discussed in this module in the section "Hazards to Plants and Animals Posed by Specific Elements". These toxic elements also share two general characteristics:

(1) They appear in significant concentrations in at least some untreated wastewaters of municipalities.

(2) They accumulate in soils amended with municipal wastes and, in some cases, produce toxic symptoms either in vegetation grown on that soil or in animals that eat that vegetation.

List of elements: As Table 1 is examined, note how necessary it is to designate the expected use of the water before toxic limits can be specified. This represents the diverse sensitivities of vegetation and animals.

Before toxic limits can be specified, the expected use of the water must be determined.

"Heavy Metals" and "Trace Elements": Metals having densities in excess of 5.0 are arbitrarily designated as "Heavy Metals". The list of potentially toxic elements dealt with in this module includes elements that are neither "heavy" nor "metals". Yet, sloppy nomenclature often bunches all the toxic elements together under the title "Heavy Metals".

It is also useful to note that potentially toxic elements occur naturally throughout our environment, albeit (in some instances) in extraordinarily small concentrations. All organisms, therefore, have evolved certain tolerances for these elements and, for some, a definite requirement in life processes. Because of their

Because toxic elements occur in nature, all organisms have developed tolerances for them.

TABLE 1

Eighteen Potentially Toxic Elements Identified in Two Sources

	ELEMENT	MAX. LEVEL IN DRINKING WATER (mg/l)[a]	MAX. LEVEL FOR CONTINUOUS USE IRRIGATION WATER, ALL SOILS (mg/l)[b]
As	Arsenic	0.05	0.01
Al	Aluminum		5.00
B	Boron		0.75
Ba	Barium	1.00	
Be	Beryllium		0.50
Cd	Cadmium	0.01	0.01
Cr	Chromium	0.05	0.10
Co	Cobalt		0.05
Cu	Copper		0.20
Hg	Mercury	0.002	
Mn	Manganese		0.020
Mo	Molybdenum		0.21
Ni	Nickel		0.20
Pb	Lead	0.05	5.0
Se	Selenium		0.02
Ag	Silver	0.05	
Zn	Zinc		2.0
F	Fluorine	varies with mean temp.	

[a] Train, 1975

[b] EPA, 1975b

wide occurrence in small concentrations in plants and animals, the listed toxic elements also are known as "trace elements".

So the elements listed in Table 1, along with others, are called "Heavy Metals" by some authors, "Trace Elements" by others, and "Toxic Elements" by still others. In this module, the term "potentially toxic elements" is considered more descriptive, and hence is used throughout the Land Application of Wastes program.

While all the toxic elements are potentially dangerous, some receive special attention because of circumstances surrounding their occurrence, their greater concentrations, or their impact. For example, if cadmium exceeds 1.0% of the zinc content of municipal sludges, its uptake by crops may lead to cadmium poisoning in animals eating those crops (Chaney, 1973). Similarly, high zinc or copper levels are sometimes toxic to plants ("phytotoxic"), and composted municipal refuse may be a significant source of highly phytotoxic boron. On the other hand, an element such as silver may be of only academic interest in most land application systems merely because it does not appear in significantly high concentrations.

It is generally agreed that the potentially toxic elements of untreated wastewaters most likely to pose a threat of phytotoxicity or animal toxication are boron, cadmium, zinc, copper, molybdenum, and nickel (Chaney, 1973; Leeper, 1972; Page, 1974; CAST, 1976).

Boron, cadmium, zinc, copper, molybdenum, and nickel are the elements of untreated wastewater most likely to be toxic for plants and/or animals.

Sources of Toxic Elements:

As mentioned earlier, toxic elements occur naturally throughout the environment. Toxic elements also may be added directly in the form of, say, metal-based pesticides (viz. arsenate of lead used in the past) if the site is used for growing appropriate crops. However, most toxic element increase in soils at land application sites comes from the general community through its wastewater and, particularly, its sludges.

Increase in toxic elements at land application sites comes from the wastewater and sludges of the general community.

Residential contributions: Toxic elements are present in significant concentrations even in domestic sewage (Davis and Jacknow, 1975). Presumably this represents contributions from the brass, copper, and lead of plumbing, from cosmetics, hobby materials, and from internal and external medicines. This latter category is exemplified by mercurial diuretics and dandruff preparations employing selenium. The concentration of elements commonly found in sludge from communities without excessive industrial waste inputs (or with adequate source abatement) should be no higher than 2000 mg/l for zinc and 1000 mg/l for copper, lead, and chromium. (Menzies and Chaney, 1974).

Community residents discharge significant amounts of toxic elements probably originating from cosmetics, hobby materials, medicines and particularly from metal plumbing pipes.

Special industries: Certain industries discharge toxic elements in high concentrations. Foundries, electroplating and photoengraving shops, and similar concerns often discharge iron, copper, nickel, zinc, chromium, and/or cadmium. Mercury is often associated with wastes from the electrolytic production of chlorine and caustic soda, from the manufacture of electrical equipment and antifouling paint (Hammond, 1971), and from the combustion of coal (Billings and Matson, 1972; Joensuu, 1971). The manufacture of viscose rayon, the vulcanization of rubber, or even some processes of paper production can discharge significant quantities of zinc.

Toxic elements discharged by certain industries are more highly concentrated than those discharged by other sources.

Urban environment: The major source of potentially toxic elements in municipal sewages of the larger cities appears to come from the more general environment. For example, lead from burning gasoline and other fuels, petrochemical industries, and incinerators is rainwashed into sewers in large quantities. Other contributions may come from smoke and dusts associated with smelters (copper and arsenic), from losses due to tire wear, from corrosion (especially in areas subject to acid rains), from the leaching of plant food and fertilizers from gardens, lawns, and parks, and so on. These sources will contribute more heavily to treatment plants served by combined storm/sanitary sewer systems or older sanitary sewers with large inputs of infiltration.

Major source of potentially toxic elements in municipal sewage of larger cities is from the general environment.

Relative contribution: To help assess the relative contributions of residential, special industrial, and urban environmental sources, turn to Figure 1. Note that the general pattern shown in Figure 1 does not hold for nickel. Substantial amounts of nickel do not come from residential or urban environments.

While those data of Figure 1 apply to New York City (where electroplating and photoengraving are the main industrial discharges of toxic elements to the municipal treatment system), the general pattern seems to have wide applicability. The urban environment generally contributes 10% to $\geq$ 50% more potentially toxic elements than residential areas, and residential areas often contribute more than industries. However, the discharges from industries to the wastewater collection system will be much more concentrated than those from the other sources. Pretreatment of industrial wastes is often the most effective means of correcting an imbalance in sludge composition to be applied to the land. However, industrial pretreatment programs will lead to significant toxic element reductions only if non-point discharges are comparatively low.

Pretreatment of industrial wastes can be an efficient way of reducing potentially toxic element concentrations in municipal sludge, but only if the industrial contribution is significant.

Sewages, Sludges, Soils: Concentrating Toxic Elements

The toxic element load carried by raw municipal sewages varies with city size, season, and even the time of day. Nevertheless, the major proportion of the toxic element load is removed in the sludge-forming processes associated with primary and secondary treatment. Several physical and chemical factors account for this, but what is particularly interesting is that those same general processes account for toxic element sorption by soils. By reviewing the simpler event, the uptake of potentially toxic elements by sludge, it is easier

The major proportion of toxic elements in sewage is removed in sludge-forming processes involved in primary and secondary treatment.

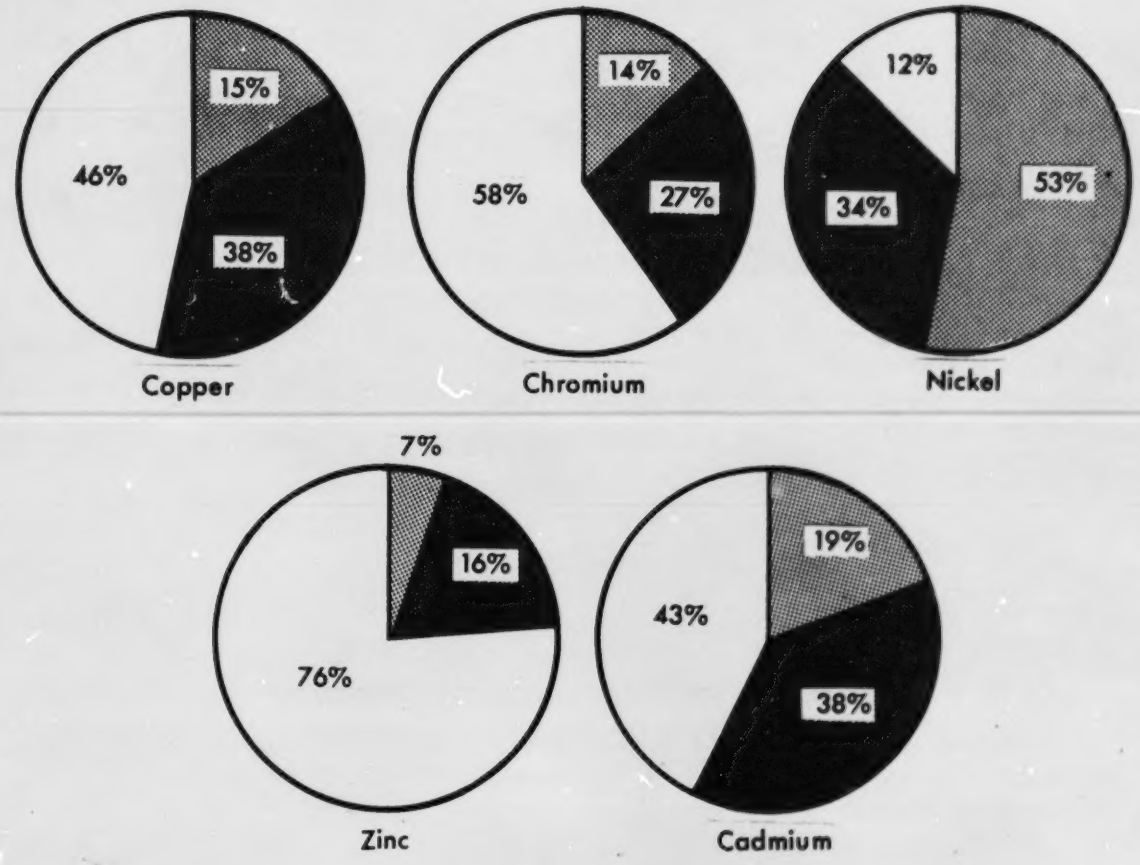

Figure 1

In municipal sewage from New York City, the major source of Cu, Cr, Zn, and Cd is from the general urban environment, with less contributed by residential outfall or even special industrial concerns (adapted from Davis and Jacknow, 1975).

to make the transition to toxic element uptake by soils.

Toxic Element Uptake by Sludges:

The uptake of potentially toxic elements by sludges is influenced by several factors, but only five will be discussed here: (1) pH, (2) ligand bonding, (3) retention time, (4) toxic element concentration, and (5) ion competition for adsorption sites. Each factor influences the attachment made by toxic elements to the solid-phase floc of sludge.

Toxic elements tend to make attachments to the solid-phase floc of sludge.

The influence of pH: The flocculant matter of sludges offers many surfaces which are negatively charged and capable of forming electrostatic bonds with cations. However, toxic elements are not the only cations in wastewaters. At low pH's the dominant cation may be the hydrogen ion (H^+). That would lead to a competition for bonding sites between the prevalent hydrogen ions and the less common ions of trace metals. In that competition, toxic element ions are at a statistical disadvantage and are not readily taken up by the sludge. Higher pH values (lower hydrogen ion concentrations) in the sewage, of course, allow for less competition and favors toxic element uptake. However, at pH's greater than 8.5, conditions also favor the direct precipitation of toxic elements as metal hydroxides. These precipitates become fixed in the biological floc and end up in the sludge. At pH's greater than 10 (common in lime precipitation for phosphorus removal) substantial precipitation of metal hydroxides occurs, particularly in zinc, cadmium, cobalt, ferrous, and ferric ions (Wood and Tchobanoglous, 1975). Representative data showing the effect of pH on the removal of nickel (Ni^{+2}) in activated sludge is given in Figure 2. Note that toxic element uptake also is dependent on the amount of active surface available as represented by the concentration of mixed liquor suspended solids.

Higher pH values in sewage during conventional treatment favor uptake of metal ions into sludge.

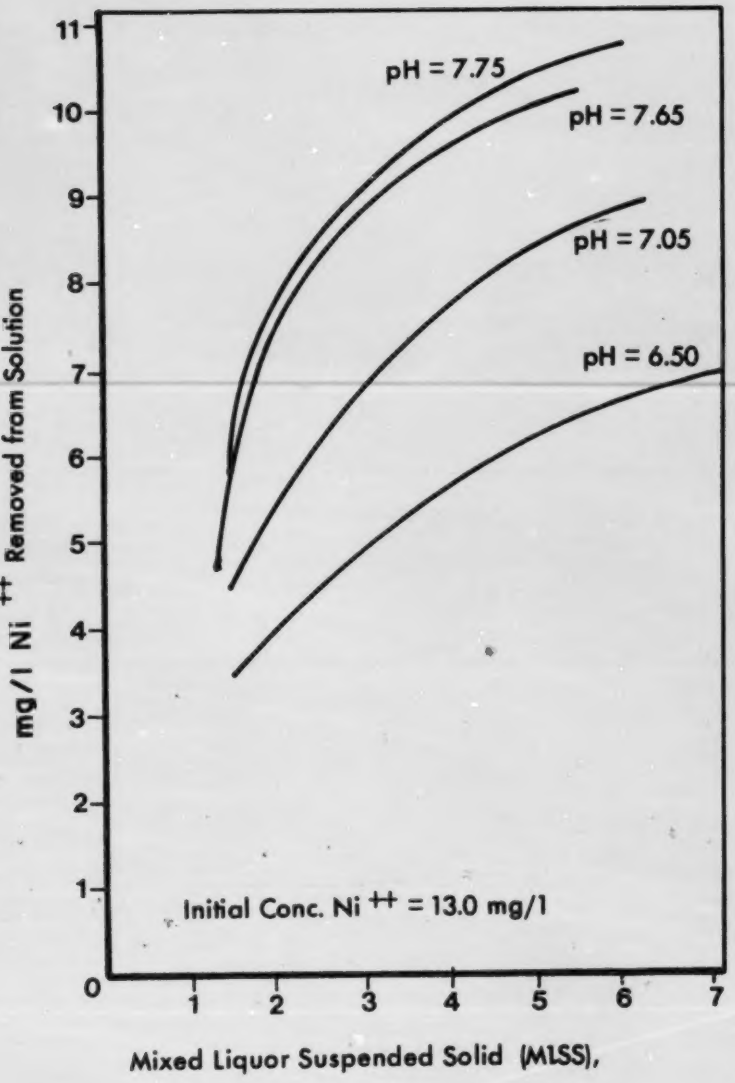

Figure 2
The uptake of Ni^{+2} by sludge increases with pH and available reactive surface (adapted from Cheng, et al., 1975).

Ligand bonding - chelation: Both dissolved and solid phases of the sewage organic matter may have chemically active sites capable of forming one or more coordinate covalent bonds with the toxic elements.

A single organic molecule capable of forming two or more coordinate covalent bonds is called a chelate. Chelating agents may react with toxic elements forming complexes that may be either insoluble or soluble. Thus, chelating agents may serve to retain toxic elements in the wastewater, blocking their accumulation in sludges, and preventing further chemical reactivity after application to soil, the organic chelate itself may be degraded and the toxic element released.

Chelates in sewage act to retain toxic elements in the wastewater and prevent their accumulation in sludge. However, after wastewater is applied to soil, the toxic element may be released.

Retention time: The uptake of potentially toxic elements by biological floc is somewhat dependent on the nature of the element, but in general, reaches a near steady state after from one to two hours of retention. This is illustrated in Figure 3.

Toxic element concentration: The uptake of toxic elements by biological floc increases with ion concentration and is adversely affected only by very high ion concentrations ($>$ 300 mg/l). Data are scarce, but the effect (if any) of very high concentrations seems to be a decrease in quantity of uptake. This is also illustrated in Figure 3.

Ion competition for adsorption sites: Toxic elements compete for reaction sites on the biological floc, with some ions showing stronger affinities than others. This can be specific to the system under investigation, and underscores the need for chemical analysis of any wastewater or sludge which must be treated.

Toxic Element Retention in Secondary Effluent:

As the factors discussed in the preceding paragraphs indicate, most of the toxic element loads of untreated wastewaters accumulate in sludges. A question remains: What is the toxic element load carried by primary and secondary effluents?

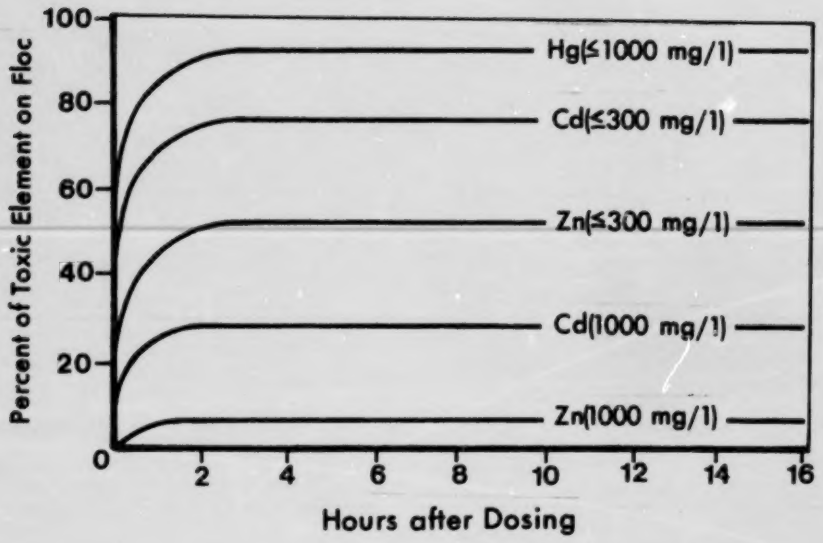

Figure 3. Uptake of toxic elements by biological floc is near steady state after two hours at any concentration, but is suppressed for some ions after higher dosing concentrations (adapted from Neufeld and Hermann, 1975).

The answer, assembled in Figure 4, is quite revealing. With only one minor exception (primary effluent, lead ion), the reported toxic element concentrations in both primary and secondary effluent are below maximum contaminant standards set by EPA for both drinking and irrigation waters. Clearly, the major concern for potentially toxic element concentrations lies in sludges, not in secondary effluents. Table 2 illustrates this point. On occasions the toxic element concentration of sludges are almost as rich as ores. However, commercial reclamation may be precluded by the chemical form of the elements.

Concentration of toxic elements is not a concern in primary and secondary effluent; the concern is with sludges.

Accumulation of Toxic Elements in the Soil:

After sludge application, potentially toxic elements become available for soil reactions through a variety of processes. For example, the environmental change may cause certain chemical complexes of the sludge to dissolve. Also, the organic matter of biological flocs and chelates may decompose, releasing toxic elements from the sludge. Even competitive reactions, involving soil constituents, may occur, forcing the desorption of toxic elements from the sludge. Whatever the mechanism of release from sludges, the elements then react with soils.

Potentially toxic elements are released into the soil by a number of mechanisms following sludge application.

It is important to note that the solid matter of soil is analogous to the surface presented by sewage sludge. As is the cases with sludges, effective uptake of toxic elements in soils depends on the pH of the soil solution, the availability of adsorption sites and ligand bonding (soil clay and humus), the relative competition that occurs between toxic elements, and the rate of flow of solutions through the soil. Other significant reactions such as precipitation and methylation also occur in soils.

Uptake of toxic elements by soil depends on pH of soil, availability of adsorption sites, competition among toxic elements, and rate of flow of solution through soil.

For convenience, this discussion will separate reactions of toxic elements into two categories: (1) reactions with soil solid matter and (2) reactions within the soil solution.

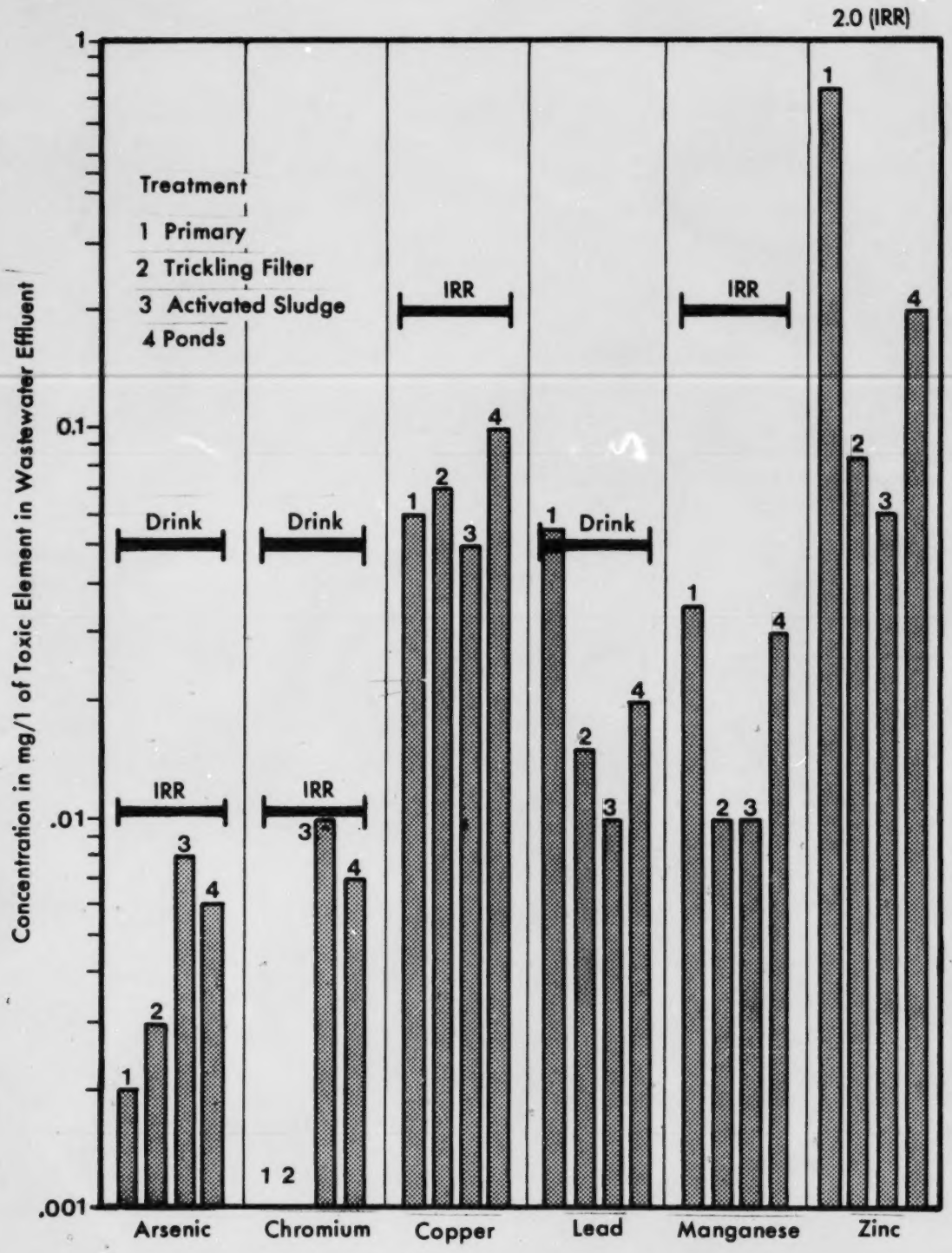

Figure 4

Toxic element concentrations in primary and secondary effluents are below EPA standards for drinking and irrigation water (adapted from Pound & Crites, 1973; Train, 1975)

TABLE 2

The Toxic Element Concentrations of Dry Sewage Sludge Greatly Exceeds that Found in Secondary Effluent (adapted from Baker and Chesin, 1975)

ELEMENT	SEWAGE SLUDGE (mg/kg dry wt) RANGE[a]	RANGE[b]	RANGE[c]	SECONDARY EFFLUENT RANGE[d] (mg/1)
Arsenic	1-18			0.003-0.008
Chromium	20-41,000	143-1,498	200-9,100	0.001-0.01
Copper	52-11,700	872-1,718	360-10,300	0.05-0.1
Lead	15-26,000	239-3,407	220-3,500	0.01-0.02
Manganese	60-3,900			0.01-0.03
Zinc	72-49,000	1,053-6,540	1,300-21,200	0.06-0.2

[a] Page, 1974

[b] Baker and Hornick, 1974

[c] Regan and Peters, 1972

[d] Pound and Crites, 1973

Reactions with soil solid matter: Three specific interactions between soil solid matter and toxic elements will be reviewed here: (1) selective adsorption, (2) covalent and ligand bonding, and (3) reversion processes.

Selective adsorption is a process of adsorption of cations that occurs on the surfaces of soil colloids (clay and humus). An overview of this process is given in Module 3, "Soil as a Treatment Medium". The total amount of toxic element removed from the soil solution by this process is not great, but it is most efficient when the soil pH is maintained at 6.5 or greater.

A small amount of toxic elements is taken up by soil solids through selective adsorption of cations. Such adsorption is not permanent nor does it prevent some uptake by plant roots.

This first adsorption of cations is neither permanent nor sufficiently protective of vegetation. Roots take up some fraction of adsorbed cations. Further, desorption, or displacement from the colloids, may occur when the ion concentrations of soil solutions change. However, such desorption is not likely to lead to toxic element "breakthrough" to groundwater unless the soil is acid, of low C.E.C. and with strongly acid and sandy subsoils (Chaney, 1974).

Covalent and ligand bonding incorporates ions in the chemically complex organic matter of the soil. This seems to be the major process removing toxic elements. Some organometallic complexes, such as Cu-organic matter, are insoluble and immobile, but others seem quite the opposite. For example, it is thought that some potentially toxic elements are made more available to vegetation after forming chelate complexes with soil organic matter.

Toxic elements are removed primarily by covalent and ligand bonding; the organic complexes formed may be soluble or insoluble.

Reversion is a slow process, often extended over a period of years, by which toxic elements are converted to highly stable chemical forms accessible to neither the soil solution nor vegetation uptake. In general, the amount of toxic element that a soil can immobilize depends on the cation exchange capacity of the soil,

Through the slow process of reversion, toxic elements are rendered inaccessible to both the soil solution and vegetative uptake; they are converted to highly stable chemical forms.

but because clay minerals differ in structure, specific predictions are very hard to make. Probably reversion does not account for more than 10 to 20% of the total adsorption capacity attributed to the mineral portion of the soil. The adsorption capacity due to soil organic matter is irrelevant with respect to this process: humus lacks the crystal lattice needed for immobilization by substitution.

Whatever reversion procedure is experienced, there is ample evidence that a radical alteration in environmental conditions (for example a significant drop of soil solution pH) may release at least some of the immobilized cations.

Interactions in soil solutions: Two specific interactions which occur outside the solid particles and hence in soil pore space are: (1) precipitation and (2) methylation.

Precipitation was discussed earlier as a mechanism by which toxic elements are removed from sewage solutions and incorporated into sludges. The principal cause of the precipitation there was the high pH which allowed the formation of insoluble hydroxides. Similarly, in highly alkaline soils, toxic elements may be precipitated as hydroxides. However, other chemical forms, such as sulfides and phosphates (to name a couple), also are precipitated within soil pores.

In highly alkaline soils, toxic elements may be precipitated as insoluble hydroxides and as other chemical forms within the soil pores.

It is important to recognize the limitations of precipitation as a mechanism for immobilizing toxic elements. First of all, standard solubility constants (K_{sp}) only describe equilibrium conditions, giving no information on the rate of precipitate formation. A salt may have a very low K_{sp} yet the time for reaching equilibrium may be much longer than the time required to pass through the land application site. Finally, it must be remembered that soil organic matter will interact with much of the toxic element in solution,

chelating it and thereby preventing the formation of inorganic salts.

There is no correlation between availability of toxic elements to vegetation and their solubility in the soil solution; highly insoluble compounds can provide more of a given element to plants than highly soluble forms.

Contrary to "common sense", the availability of toxic elements to vegetation is not correlated with solubility in the soil solution. Data of Lindsay (1972), Boawn, et al. (1957), Giordano and Mortvedt (1969), and others indicates that even highly insoluble compounds can provide as much toxic element to plants as highly soluble compounds. For example, if equal amounts of zinc as the soluble sulfate and insoluble carbonate are made available to vegetation, 8% more zinc is absorbed from the zinc carbonate even though it is about five orders of magnitude less soluble than zinc sulfate. Zinc oxide is six orders of magnitude less soluble than zinc sulfate yet delivers 67% more zinc to vegetation. Similar apparent discrepancies are reported for copper and nickel.

Methylation is one of many possible reactions associated with the metabolism of soil bacteria. The familiar example usually cited is methylation of mercury. At one time it was thought that discharges of free mercury to rivers and lakes were harmless. Since the mercury was insoluble, it was expected to settle in the mud and remain immobilized. However, under anaerobic conditions at around pH 7.0, specific microorganisms metabolize free mercury and produce monomethyl (CH_3Hg^+) and dimethyl [$(CH_3)_2Hg$] mercury, phenyl mercurials [$C_6H_5Hg^+$ and $(C_6H_5)_2Hg$] and methoxyethyl mercury [$CH_3O(CH_2)Hg^+$), all of which are very toxic and, more importantly, very soluble (Goldwater, 1971). Since other toxic elements also are known to undergo methylation, and since methylated elements often are both water soluble and very toxic (especially to higher animals), the real hazards of this event relative to land application will have to be more completely resolved. At present, not even the extent of mercury methylation in soil, much less

The potential hazards of toxic element methylation must be determined in land application; toxic elements which undergo methylation are water soluble and can be very toxic in an aquatic environment.

its potential hazard, has been fully documented. However, it is felt that this process poses a much greater threat to aquatic than terrestrial systems.

Potentially Toxic Elements in Soil, Vegetation, and Animals

Earlier, while introducing potentially toxic elements, two very significant points were touched upon lightly. One was that toxic elements occur naturally in soils. The second point was that organisms take in toxic elements but have evolved a certain tolerance for them. The following discussion returns to those themes.

Toxic Element Load of Natural Soils:

In Module 18, "Monitoring at Land Application Sites", it is argued that monitoring of a site should begin months before the site goes into operation. Clearly, since all soils naturally carry certain amounts of various elements, pre-operation monitoring of soils provides baseline data against which future accumulations can be gauged. While each site is, of course, different with respect to actual content of potentially toxic elements, some representative values are given in Figure 5.

Soils at a land application site should be monitored for toxic elements months before operation begins to determine naturally occurring amounts.

Uptake of Toxic Elements by Vegetation:

Solubility vs. availability: Earlier in this module it was argued that there simply is no definite way to specify what percentage of the total potential toxic element concentration is available for vegetation uptake. However, it has become popular to use solubility in 0.1 N HCl as an approximate estimate of availability of toxic elements to vegetation. Also, it is generally agreed that the addition of toxic elements alone would be more likely to cause plant damage than equivalent amounts in sludges, at least on a short term basis (Brown, 1975).

The percentage of the total potentially toxic element that is available for vegetation uptake cannot be specified.

Variables affecting uptake: The uptake of toxic elements by vegetation is not consistent from species to species or even in varietal forms within a species.

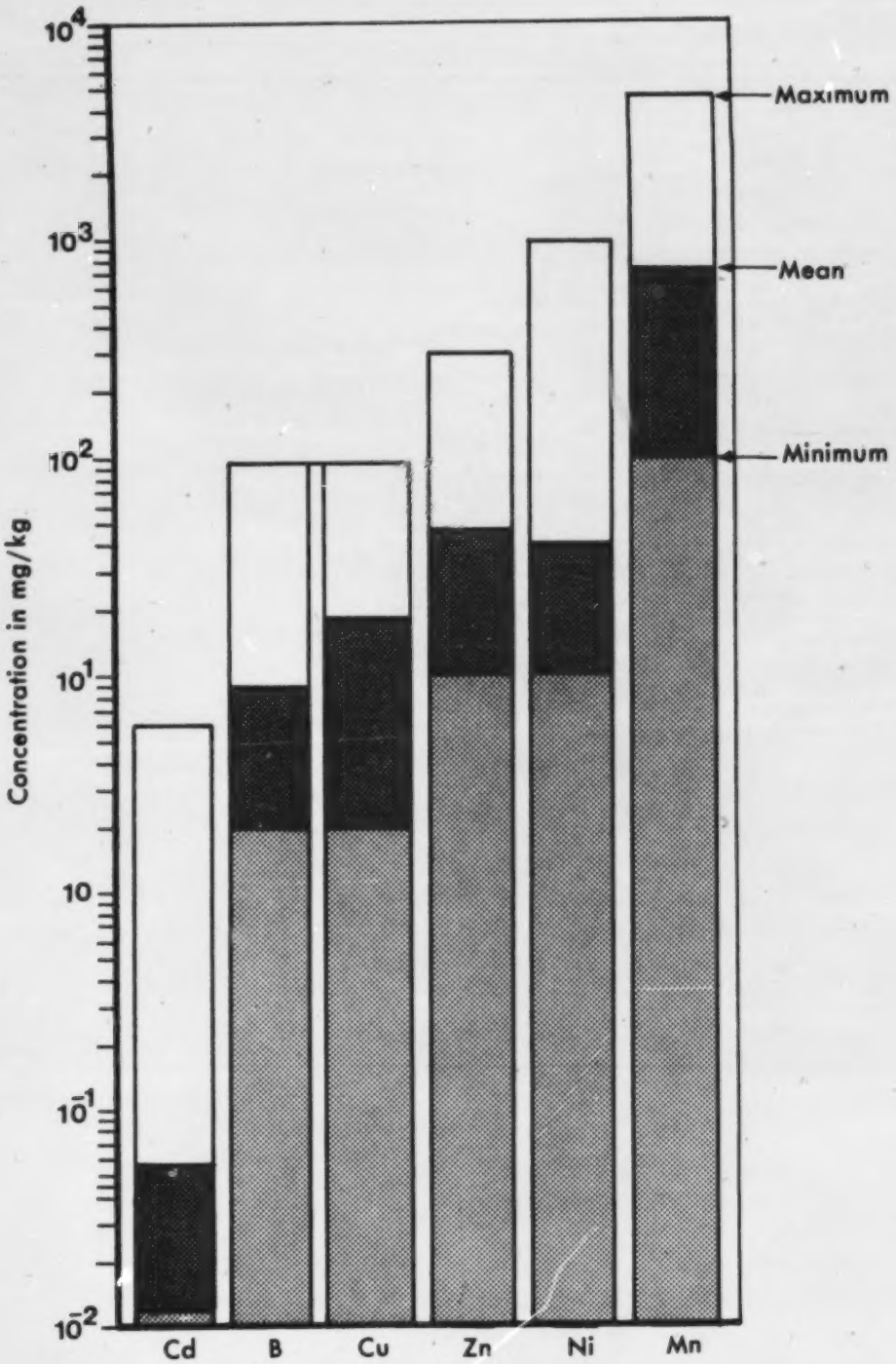

Figure 5

The range of naturally occurring toxic elements in soils (extractable with 0.1 N HCl) extends over six orders of magnitude (adapted from Alloway and Davies, 1971).

Nor are toxic elements evenly distributed throughout the plant. Depending on the plant species and the toxic element, element concentrations may accumulate preferentially in leaves, stalks, roots, or less commonly in grain. Finally, the increased concentrations in plant tissue usually are not proportional to the amount of toxic element added to the soil.

Increased concentration of a toxic element in plant tissue usually is not proportional to the amount of the element added to the soil.

Crops Associated with Land Application Practices

The crops most likely to be grown must be considered in evaluation of alternative sites. For residues containing fairly high levels of potentially toxic metals, use of the site for production of annual seed crops such as corn harvested for grain with the crop residues left in the field tends to minimize potential hazards. Use of the site for production of leafy vegetables provides much less protection from potential hazards.

Plant species and even varieties differ widely in tolerance to toxic metals. Vegetable crops that are very sensitive to toxic metals include the beet family (chard, spinach, redbeet, and sugarbeet), turnip, kale, mustard, and tomatoes. Beans, cabbage, collards, and other vegetables are less sensitive. Field crops such as corn, small grains, and soybeans are moderately tolerant. Most grasses, (fescue, lovegrass, Bermudagrass, orchard grass, perennial ryegrass, etc.) are tolerant to high amounts of metals.

Uptake of toxic elements varies according to plant species and even plant variety.

At excess levels, the grain, fruit, or edible root of many crops contains two- to tenfold lower levels of Zn than the leaves. Thus, corn grain from a sludged site could contain less toxic metals than mixed pasture or silage. Whether the relative exclusion of toxic metals by grasses would allow more nutrient removal,

Toxic elements may accumulate preferentially in leaves, stalks, roots, and less commonly in grain.

yet safer levels of Zn, Cd, and Pb, than growth of corn grain is unclear. A further advantage of grain crops vs. leafy crops is the two- to tenfold greater exclusion of Cd relative to Zn during grain filling.

Some have suggested that we should breed varieties of crops that can tolerate and exclude undesired toxic elements. Although more tolerant varieties probably could be developed, only an effort to produce metal-tolerant perennial grasses that would exclude toxic elements seems reasonable for using field crops in waste application sites. This would allow maintenance of an economic crop on sites dedicated to receive sludge or effluent after other economic crops would no longer be grown due to the soil toxic element levels. Properly designed advance studies and monitoring can be used to divert some sludges that are high in potentially toxic elements to sites that are used for ornamental plants, fiber crops, or other uses that do not involve a potential hazard to food chains. The problem of land application of sewage sludge will be most severe for large industrialized cities with a limited range of potential application sites. In extreme cases, some method such as incineration may be more feasible than land application. It should be recognized, however, that the hazard to food chains from potentially toxic elements in ashes may be even more severe than from these same elements in the unburned organic material.

One management option for sludges with very high contaminant levels is to apply these wastes to non food crops such as fibers or sod.

A fuller discussion and much tabulated data on crop tolerances for potentially toxic elements and salts, as well as other factors, are included in Module 20, "Crop Selection and Management Alternatives".

Large industrial cities with limited land area for sludge application face the most difficult problem in sludge disposal.

Table 3 summarizes some known beneficial effects and potentially toxic effects of many of the elements likely to be encountered in land treatment of wastewater and sludges. The next section focuses on several of these elements for which toxic effects and/or potentials have been documented. Some management tools to minimize effects are mentioned.

Table 3

EFFECTS OF SELECTED ELEMENTS ON PLANT AND ANIMAL NUTRITION

Element	Comment	Behave as Essential or Beneficial Elements		Behave as Toxic Elements	
		Plant	Animal	Plant	Animal
B	narrow margin	yes	no	yes	
Ca		yes	yes		
Cl		yes	yes	yes	
Cr	activates insulin	no	yes		
Co	B_{12}, n-fixation		yes		
Cu	toxic to sheep if Mo < 0.1 ppm	yes	yes	yes	10-20 ppm*
F	tea only crop with uptake	no	yes	yes	yes
I	once common animal deficiency	no	yes		
Fe	most common animal deficiency	yes	yes	pH < 5	
Mg	deficiency causes grass tetany	yes	yes		
Mn	toxic in acid soils	yes	yes	pH < 5	
Mo	induces Cu deficiency	yes	yes		5-20 ppm*
P	most critical mineral deficiency	yes	yes		
K	contributes to Mg deficiency	yes	yes		
Se	may be deficient or toxic	no	yes		4 ppm*
Si	may interfere with digestion	yes	yes		yes
Na	vegetable diets often lack Na	Some	yes	yes	
S	cystine, dysine, methionine	yes	yes		
Zm	lacking in some U.S. diets	yes	yes	yes	
Ni		no	maybe	yes	possible
Sr			maybe		
Sn			maybe		
V			maybe		
Al		no	no	pH < 5.5	

Table 3 continued

As	phytotoxic before animal toxic	no	no	yes	yes
Cd	counteraffected by Zn and Se	no	no	yes	yes
Pb	hazard primarily surface deposition	no	no		yes
Hg	aquatic accumulation	no	no		yes

Source: Adapted from Allaway (1968), Walsh, et al. (1976), and Allaway (1977)

*concentration (ppm) at which vegetative dry matter may be toxic to consuming animals.

Specific Elements Pose Hazards to Plants and Animals

In this section potentially toxic elements are grouped according to the relative risk of toxicity to plants or animals. Conditions which favor or hinder their availability to plants and animals are also discussed. Most of the information in this section comes from two reports, "Food Chain Aspects of the Use of Organic Residues" (Allaway, 1977) and "Application of Sewage Sludge to Cropland" (Council for Agricultural Science and Technology - CAST - 1976).

Elements posing relatively little hazard are:

- -Aluminum
- -Antimony
- -Arsenic
- -Chronium
- -Fluorine
- *-Iron (discussed with aluminum)
- -Lead
- *-Manganese (discussed with aluminum)
- -Mercury
- -Nitrogen
- -Selenium
- -Zinc
- -Other Elements

Elements posing a potentially serious hazard are:

- -Boron
- -Cadmium
- -Copper
- -Molybdenum
- -Nickel

This classification of the potentially toxic elements into groups of "relatively little hazard" and "potentially serious hazard" assumes that good management practices are in effect at the application site. It applies to elements entering the food chain through plant roots rather than by ingestion from plant or soil surfaces by grazing animals.

Relatively Little Hazard

Aluminum, Iron and Manganese: The levels of these three elements in sludge usually will not be of any environmental concern. Levels of Al, Fe, or Mn may be high in sludges from tertiary treatment processes, but they will not be a limiting factor in sludge application rates if the soil pH is maintained above 5.5 and the soil is well aerated. Soil pH is the most important control. Below pH 5.0, aluminum toxicity is common in plants, and excessive manganese may be taken up if it is present in the soil. At low pH levels, high availability of iron can induce plant manganese deficiency.

Aluminum, iron, and manganese will not be toxic as long as low pH is avoided and good aeration of soil is maintained.

Well-aerated soils are important to avoid reducing conditions. Both manganese and iron are more soluble in a reducing environment.

Antimony: Antimony is not known to be an essential element for plants, but it has been reported to be moderately toxic. Antimony is sorbed very strongly by kaolinite and sesquioxides under acid conditions, but appears to move freely in neutral to alkaline soils. Antimony generally occurs in sewage sludge in very low concentrations, and although it could be a hazard to plants and animals at high concentrations, there is no evidence currently available of a hazard.

Antimony usually occurs in sludges at very low concentrations.

Arsenic: The use of organic arsenicals in poultry feeds is the principal source of As in organic wastes. Concentrations of 15 to 30 ppm As have been reported in poultry house litter (Morrison, 1969). Where poultry litter of this type had been applied to soils for as much as 20 years, no increase in the As concentration in alfalfa and clover was detected.

Although there are fewer data on As concentration in municipal sewage sludges than for many of the other trace elements, Page (1974) gives a range of 1-18 ppm As in some sludges from Michigan.

Predictions of the hazard from As in organic materials must be derived from experiments on As residues from pesticides. The fate of As from pesticide residue has been discussed by Woolson, in terms of accumulation of As in soils. Crop failure, or sharply diminished yields, usually precede the production of crops that have hazardous levels of As in the edible portion.

Soil tests for predicting the hazard of phytotoxicity of As residues have been developed (Woolson et al, 1971). Use of these tests to monitor As accumulations and prevent development of phytotoxic levels offers substantial protection against food chain damage from As in organic materials.

Tests to monitor arsenic accumulations in soil provide protection against its damaging the food chain.

Chromium: Chromium is not expected to be a limiting factor in determining the quantity of sludge that may be applied to agronomic soils because a) plants can tolerate relatively high levels of chromium applied in sludge; b) plants do not accumulate chromium even when it is present in the soil at high levels; c) there is evidence that chromium is required by humans and animals and that diets are deficient in chromium in certain areas (Underwood, 1971).

Little soluble chromium is found in soils, because when added in the soluble trivalent form it rapidly is transformed to insoluble forms, probably hydroxides or oxides. Hexavalent chromium is toxic to plants, but it is reduced to the trivalent form in sludge digestion. In view of the limited possibility for hexavalent Cr to be present in organic materials, it appears that Cr in these sludges presents no hazard to food chains.

It appears that chromium in sludges presents no hazard to food chains.

Fluorine: Fluorine is probably essential to animals, but can be toxic to plants and animals at high concentrations. The hazard of fluorides in organic residues is apparently minor and confined to sludges containing soluble fluorides when applied to strongly

acid soils. Liming to higher pH can substantially correct any F difficulties.

Lead: The most surprising fact about Pb in soil is its apparent concentration in a profile in greatest amounts at the surface with the organic matter. This is the product of two causes; first, that some plants absorb it in substantial amounts; second, that it is very strongly fixed by soil. The chemical mechanism of fixation by soil is that Pb^{2+} is hydrolyzed and polymerized, and is more tightly bound as pH rises. In accordance with this tight holding by the soil, the Pb extracted with dilute acetic acid does not show the high surface values shown by the total mass balance of Pb through the soil profile.

Where the organic residue is incorporated into the soil, Pb contained in the residue appears to offer very little hazard as far as toxicity to humans and animals are concerned, and only a modest toxicity to plants (Baumhardt and Welch, 1972). Lead added with sludge is not phytotoxic because the sludge contains a large amount of phosphate which ties up Pb and prevents injury to plants, which would result from their uptake of Pb. On soils that have been treated with as much as 3200 kg/ha of Pb in the form of soluble salts, the concentration of Pb in corn leaves was increased but the Pb concentration in the grain was unchanged. Therefore, production of crops where only the edible seed is harvested may be an effective way of preventing Pb toxicity to humans and animals. Uptake of Pb by plants may also be reduced by liming acid soils. In general, potentional hazards of Pb toxicity are reduced whenever the Pb is incorporated in soil, in contrast to the potential hazards from atmospheric Pb.

Hazards of lead toxicity are reduced when it is incorporated into soil as contrasted to hazards from atmospheric lead.

Mercury: Such experimental evidence as we have of Hg shows that the metallic ion is strongly held by soil and is not absorbed by plants. The amounts of the element in circulation are far smaller than those

elements posing a potentially serious hazard, so the mechanisms of adsorption within the soil will never approach saturation.

Concern over hazard to food chains from Hg in sewage sludge has stemmed from evidence of methylation of Hg in aquatic systems, and from recent episodes of methylmercury poisoning from inadvertent human consumption of treated seeds. More recent research has indicated that the Hg concentration in above-ground parts of plants is generally very low, even though Hg seed treatments or other additions of Hg to soils had been made. Chaney (1973) indicates that hazards from Hg in terrestrial food chains are much less than those in aquatic food chains.

Mercury concentration in above-ground parts of plants is generally very low. Mercury poses no threat to groundwater.

Organic and inorganic mercury compounds may decompose to elemental mercury, then volatilize or form compounds with sulfide and chlorides. Because of its high affinity for solid soil surfaces, mercury persists in the upper soil layer and is not a threat to groundwater.

Nitrogen: Problems associated with N in organic wastes include the hazard of high nitrate concentrations in crops, drainage water, and groundwater, including the possibility of nitrosamine formation. Cattle can be affected by grass tetany, as described in Module 20, "Crop Selection and Management Alternatives".

There is no evidence that N in organic wastes presents either more or less hazard than equivalent amounts of nitrifiable or plant-available N from inorganic sources. The objectives of management of N in organic waste application are to provide needed amounts of N to the crop, to avoid production of crops high in NO_3^-, and to minimize NO_3^- accretion in water. The hazard from high NO_3^- crops can be minimized by growing corn or other cereals for grain. Cereal seeds have not been found to contain high levels of NO_3^- even

Management objectives for nitrogen are to provide needed amounts for crops, avoid producing crops high in NO_3^-, and minimize NO_3^- accretion in water.

when the leaves and stems contain hazardous levels. Where appropriate crops and crop uses are selected, potential for NO_3^- accumulation in waters constitutes the major criterion for safe application of N in organic residues to farm lands.

Nitrogen is the limiting factor in most land application situations. It is discussed in depth in Module 15, "Nitrogen Considerations", and mentioned in connection with system design at several other points in the modules.

Selenium: Selenium is essential for animals and probably for people, but not for plants. Concentrations of about 0.04 ppm Se or more in diets are required in order to prevent Se deficiency in young animals. Higher concentrations of dietary Se are toxic to animals, and a dietary concentration of less than 4 to 5 ppm is often suggested as the maximum amount that will avoid Se toxicity. Both Se deficiency and Se toxicity are problems of practical importance in livestock production in the United States and in other countries. There are a number of recent reviews describing nutritional effects and environmental cycling of Se (Underwood, 1971; National Academy of Sciences, 1971; Allaway, 1973).

Both selenium toxicity and deficiency pose problems to livestock producers.

The potential value and potential hazard of Se in organic residues are influenced by the stability and biological activity of different forms of Se. The Se in manures and sewage sludge is very likely to be present as elemental Se, selenites strongly bound to hydrous iron oxides, heavy metal selenides, or trimethylselenonium salts. All of these compounds are of very low availability to plants or animals, and when incorporated into soils they are rarely taken up in potentially toxic concentration by plants. Special care must be taken to avoid concentrations of Se which are phytotoxic for such conditions would be a serious threat to the food chain. There appears to be a minimal hazard to food chains from Se in organic residues, and

The selenium compounds found in sludges are of low availability to plants and animals; selenium is most readily available in alkaline soils.

minimal opportunity to improve the nutritional quality of very low Se crops through organic residue utilization practices. Selenium is, however, most readily available in alkaline soils.

Zinc. Zinc is the most abundant, and most valuable in terms of nutritional quality to crops, of the trace elements in organic residues. Zinc deficiency in crops has been noted with increasing frequency in recent years, and it has been suggested that some of this increase is due to feed crop removal without use of animal manures (Viets, 1966). Application of animal manure to the cut areas in fields leveled for irrigation in order to correct Zn and iron deficiency is a common practice.

Zinc deficiency in livestock, especially hogs, is a problem of long standing and there is evidence of Zn deficiency in people in many countries, including the United States (National Academy of Sciences, 1974). Zinc deficiency of people and animals is frequently associated with low availability or digestibility of dietary Zn rather than with low total Zn intake. Zinc from plant sources, and especially Zn in seed plants seems to be of lower digestibility than the Zn in foods of animal origin. However, the concentration of digestible Zn in seed crops can be increased through increase in the supply of available Zn to the plant (Welch, et al., 1974).

Zinc is a nutritionally valuable element which is deficient in many animals and humans.

Zinc is more toxic to plants than to animals or humans. One of the recent examples of phytotoxic effects of Zn contained in liquid sewage sludge has been described by King and Morris (1972). In this instance, the yield of rye declined whenever rye foliage contained concentrations of Zn of about 500 ppm or more. Levels of dietary Zn of this order and higher have been fed to animals with very little evidence of ill effects (Underwood, 1971). Therefore, it appears safe, as pointed out by Chaney (1973), to assume that phytotoxicity of Zn provides safeguard against extensive production of food or feed crops that may contain Zn concentrations that would be hazardous to consumers of these crops.

Phytotoxicity provides a reliable barrier to toxic Zn levels in food and feed crops.

The factor of phytotoxicity is particularly significant to the control of another metal, Cd, in the food chain. By maintaining a Cd/Zn ratio of 1:100 in sludges or irrigation waters, heavy metal accumulations of Cd and Zn in soil will lead to phytotoxic conditions due to Zn before Cd concentration can become detrimental to the food chain. Cd is also toxic to plants, but Cd can reach unacceptable levels in the food chain before its phytotoxic levels are reached.

Maintaining a Cd:Zn ratio of 1:100 is a widely used management practice designed to prevent the production of food crops with toxic Cd concentrations.

Heavy applications of organic residues that are high in P and relatively low in Zn may lead to Zn deficiency in crops from phosphate-induced Zn deficiency (Viets, 1966).

According to studies by Giordano and Mays (1976) and Touchton, et al. (1976), the availability of Zn is reduced more by liming than is that of Cd, Cu, or Ni.

Other elements posing potential hazards. In addition to the elements discussed above, there are many other elements that can be present in municipal sewage sludge or effluents. Some of these elements undoubtedly pose potential hazards to food chains, but the extent of and possible procedures for minimizing these hazards have not been worked out. The potentially hazardous elements include strontium, lithium, beryllium, antimony, vanadium, bromine, iodine, tin and probably others. Some of these elements, especially iodine, may have beneficial effects on the nutritional quality of crops unless application rates of residue and iodine uptake by plants reach excessive levels.

Many other elements that can be found in sewage from industrial cities may pose hazards to the food chain; monitoring of a large number of elements in sludge is recommended.

It must be recognized that most of the elements could be present in sewage from industrialized cities. Therefore, an effective monitoring system that measures concentration of a very large number of elements in sewage sludge is essential to the use of these sludges in food crop production.

Potentially Serious Hazard

Boron. Problems with B are likely to be confined to soluble B compounds in sewage effluents. Composted municipal rubbish is another source of B. Boron is not required by animals and is of low toxicity to them. The first impact of application of high B effluents to agricultural soils is reduced crop growth due to B toxicity. Boron injury to plants caused by irrigation with high boron sewage effluents was noted in the U.S. as early as 1928. Techniques for evaluating the B status of soils and plants are described by Bradford (1966). Alkaline soils used for production of B-tolerant crops represent the best conditions for minimizing the hazard of phytotoxicity from high B effluents.

The first effect of high levels of boron in effluents is to reduce crop growth due to boron toxicity.

Alkaline soils and B-tolerant crops minimize the hazard of boron phytotoxicity.

Boron in excess can injure plants. Boron in effluents could become phytotoxic in soils where we are not concerned about the B content of normal irrigation water.

Use of high B effluents as sources of B to meet plant requirements on low B soils is of uncertain value due to the narrow margin between B requirements and B toxicity for plant species. Only effluents containing very constant levels of soluble B could be used in this way.

Cadmium. Concern over Cd in foods stems primarily from the experiments and writings of Schroeder and his associates (1964), plus the itai-itai disease occurrence in the Jintsu Valley of Japan (Kobayashi, 1971). Schroeder's work carried the implication that dietary Cd might accumulate in the kidneys and lead to hypertension. In itai-itai disease, a very painful disintegration of bone was evident.

Recent reviews of the Cd problem (Fleischer et al., 1974; National Academy of Sciences, 1974) show that adverse effects of dietary Cd upon human health are not clearly established. Although workers in Cd industries are subject to respiratory diseases, excessive incidence of hypertension among these workers has not always been found. Itai-itai

disease appeared to have affected only that part of the population most likely to be deficient in calcium or Vitamin D.

Even though detrimental effects upon people or animals of Cd contained in organic materials have not been established, there is still a high level of concern over this problem, and more research effort has probably been directed toward Cd than toward any other trace element in municipal sewage sludge. Even so, differing opinions on the potential hazard of Cd in sewage sludges continue to appear. The following points are relevant to analysis of this problem:

Cd is of great concern as a potential health hazard in humans and animals, but opinion differs on the potential hazard of cadmium in sludges.

(a) Although many municipal sludges are low in Cd, some from industrialized cities contain more than 500 ppm Cd (dry basis) (Page, 1974). Sludges containing more than 500 ppm Cd are probably quite rare in that levels in this range may be associated with sterilization of digesters (Regan and Peters, 1970). Chaney (1973) reports an observed range of 5-2000 ppm Cd in sewage sludge.

(b) Current background levels of Cd are probably about 0.05 to 0.40 ppm in human diets and the average daily human intake of Cd is probably 40 to 150 µg/day. Cadmium intake of people affected by itai-itai disease may have been 600 to 1000 µg/day. Vegetables containing over 40 ppm Cd have been collected in places where pollution by airborne Cd has occurred. (National Academy of Sciences, 1974).

(c) Levels of Cd found in plants grown on field soils treated with sewage sludge, including some sludges containing over 200 ppm Cd, have been substantially lower than those in plants exposed to airborne Cd, or in plants grown in soils or culture solutions containing added organic Cd (Chaney, 1973; John, et al., 1972; Jones, et al., 1973; Page, et al., 1972). Similarly, Cd contained in foods of plant origin is very likely less digestible, and therefore less hazardous, than equal amounts of Cd in soluble inorganic forms contained in water or inhaled as dusts.

(d) The ratio of Zn to Cd in plant material grown in unpolluted areas, and in human diets is usually in the range of 100 to 1. Under some circumstances Zn competes with Cd in uptake and translocation processes in plants. Dietary Zn may also decrease the toxicity of Cd in animals. Similar protection against Cd toxicity may be afforded by dietary selenite (National Academy of Sciences, 1974).

Zinc, and possibly selenite, can compete with Cd in plant uptake. Cd toxicity may also be lessened in animals by this competition.

(e) Plant species vary widely in their tendency to accumulate Cd added as soluble inorganic Cd compounds to soils or culture solutions. The concentration in Cd in edible seeds or fruits is generally lower than in leafy vegetables. The concentration of Cd in the kernels of corn has been especially low, even when the corn is grown in soils treated with heavy rates of high Cd sludge (Chaney, 1973).

Cd tends to concentrate much less in fruit and seeds than in leafy vegetable tissue.

The most important feature of any program for minimizing the hazard of Cd from sewage sludge is probably the need for continuous monitoring of Cd concentrations in sludges and in plants growing on sludge-treated areas. Although safe upper limits of Cd in food and feed crops have not been established, uncontrolled increases in the concentrations of Cd in these crops are undesirable.

It is most important to monitor cadmium concentrations in sludges and in plants growing on sludge-treated areas.

Monitoring of Cd/Zn ratios in wastes and adjustment of these ratios to keep the level of Cd at less than 1.0% of the Zn present, selection of finer textured neutral or alkaline soils as disposal sites, regulation of annual and total application rates, and cropping the disposal site to corn used for grain are measures that help to minimize the hazard of food chains from Cd contained in sludges. In the absence of well defined values for the permissible limit of Cd concentrations in human and animal diets, it is uncertain whether or not phytotoxicity of Cd will act as a safeguard against detrimental effects of Cd in food and feed crops.

Keeping the Cd:Zn ratio at less than 1.0%, use of fine textured alkaline soils, regulation of application rates, and growing corn for grain are management suggestions where Cd may pose a problem.

Copper. Cu is adsorbed on negatively charged surfaces in soils like the other heavy metals. In two studies that have been made of its adsorption on clay minerals and

quartz, the adsorption from dilute solution has been shown to fit the Freudlich formula, $y = ac^{1/n}$, where y is the Cu adsorbed per unit adsorbent and c is the concentration of Cu in solution, a and n being constants. The adsorption is greatly increased on raising the pH, both in the above studies and in soils, so that the Cu is then more firmly fixed and thereby less toxic to plants. While added Cu is so strongly retained on acid soils that it barely moves toward the subsurface, it is still reactive enough to be toxic to plants.

Most of the present concern over Cu in organic residues stems from proposals to use relatively high (>200 ppm) levels of Cu in rations for hogs to promote growth stimulation or antibiotic effects. This use of Cu in pig rations is reviewed by Underwood (1971). The disposal of manure slurries from Cu-supplemented pigs has been studied by Batey, et al., (1972). They concluded that there was little danger from Cu toxicity in animals from use of manure from Cu-supplemented pigs unless the slurry was topdressed on a growing sward of grass. Incorporation of manure from Cu-supplemented pigs into the soil did not consistently increase the Cu concentration in forage grasses.

The Cu concentration in municipal sewage sludges is reported to range between 250 and 17,000 ppm (Chaney, 1973). Median or average values as reported by Page (1974) are frequently about 1,000 ppm. Thus the Cu concentration in municipal sludges approximate maximum values expected in manure from Cu-supplemented pigs. Copper concentrations in crops produced on land treated with municipal sludges have not been elevated to levels indicative of a hazard from Cu toxicity to consumers of the plants (Peterson, et al., 1971).

Crops grown on sludge application sites have not shown copper levels that would pose a hazard to consumers of plants.

Monogastric animals including man are not highly susceptible to Cu toxicity and the primary ill effect of diets containing 200 ppm Cu or more is ordinarily a

correctable interference with absorption of zinc or iron (Underwood, 1971). Phytotoxicity of Cu will ordinarily inhibit plant growth before Cu concentrations in this range would be found in plants.

Ruminants, especially sheep, are more susceptible to Cu toxicity and may be adversely affected by dietary Cu concentrations found in plants growing on Cu-polluted areas. This Cu toxicity can be controlled by careful use of dietary supplements of molybdenum.

Monogastric animals including man are not highly susceptible to copper toxicity; ruminants are.

Applications of Cu in organic wastes may help to prevent Cu deficiency in plants, and possibly in animals, but this is a crude and inefficient method of correcting these deficiencies.

Molybdenum: The potential hazard from Mo in organic residues is very closely related to the nature of the soils available for treatment with organic residues, to the crops produced, and to the use of these crops. Molybdenum is required by plants but the requirement is low in terms of normal nutrient application rates. Where levels of available Mo in soils are very high, plants may accumulate concentrations of Mo that are detrimental to ruminants that eat these plants. The effect of excessive Mo on animals is primarily a disturbance of Cu metabolism, and most instances of Mo toxicity can be corrected by supplementation of the animal's diet with Cu, or by use of injectable forms of Cu. Ruminants are much more susceptible to Mo toxicity than are monogastric animals. Molybdenum-Cu relationships in animal nutrition are discussed by Underwood (1971).

Molybdenum toxicity has been a serious practical problem to livestock producers in the intermountain area of the Western United States. All of the areas producing forages containing toxic concentrations of Mo are occupied by wet, alkaline or neutral soils containing relatively high levels of organic matter. Nearby well drained soils, even though formed from high Mo parent materials do not produce high Mo forages.

Molybdenum toxicity affects ruminants and is related to Cu toxicity. Wet, highly organic, neutral to alkaline soils produce the highest forage Mo content.

On the basis of the naturally occurring instances of Mo toxicity, it seems safe to assume that Mo in organic residues presents no hazard to the food chain provided that these residues are used on well drained soils with pH values of 6 or less. Where it is necessary to use high Mo residues on poorly drained alkaline soils, the use of these areas as pastures for ruminants should be discouraged, or else careful attention should be directed to Cu supplementation of the animals.

Molybdenum in sewage sludges poses no hazard to the food chain when applied to well-drained soils with a pH of 6 or less.

Nickel. Ni behaves generally like Zn, though it forms stronger chelate links with organic groups and so has some analogies to Cu. But its main characteristic is to be held on the negative surfaces, the more strongly as pH rises. As with Zn, when an added Ni salt is equilibrated with a soil for a month, the Ni can be recovered only in small amounts with the conventional ammonium acetate, but this means little. Soon after adding a Ni salt, 50% of the Ni may be recovered by ammonium acetate extraction, but if the soil was brought from pH 5.2 to 7.0 by adding lime, it recovered only 20%, which is in keeping with the lowered toxicity after heavy liming.

The role of Ni in animal nutrition has been reviewed by Underwood (1971). Nickel may soon be established as an essential element for animals, but required dietary levels are likely to be very low. Dietary Ni levels of 500 ppm or more have been fed to experimental animals without acutely toxic effects, but chronic effects of lower levels of Ni ingestion are possible. Vanselow (1966) has summarized data on Ni in plants and indicates that Ni concentrations in plants of 50 to 100 ppm dry basis are usually indicative of Ni toxicity to the plant. Most of the information on Ni toxicity to plants has been developed from studies of plants growing on soil derived from serpentine, and other factors in addition to high Ni concentrations may have been responsible for plant symptoms observed. Phytotoxicity appears to provide a

Although crop failure or sharply diminished yields precedes the production of crops containing hazardous levels of nickel in the edible portion, it is desirable to monitor sludge-treated soils for nickel concentrations.

substantial barrier against Ni toxicity to humans and animals. Monitoring of Ni levels in sewage sludge and in crops grown on sludge-treated areas is highly desirable however, since Page (1974) reports Ni concentrations in sludges of 3,000 ppm or more and cites evidence that plants grown on sludge-treated soils are substantially higher in Ni than controls.

Specific Recommendations for Sludge Application

Soil Conditions

Not every soil is suited for sludges high in potentially toxic element concentrations. Three important soil variables are texture, pH, and organic matter.

Usually, the preferred soil will be medium to fine textured and either neutral or alkaline. In all cases, soils used for food crops are expected to be maintained at pH 6.5 or above at all times during, and for two years after, application (Chaney, 1974). This recommendation will protect against toxic element mobilization through redissolving and leaching as discussed earlier. If extensive liming is needed to maintain this level of soil pH (especially pH 7 or above), there is the possibility of a Ca/Mg imbalance which must be avoided. Leeper (1972) considers soil pH to be the most important single aspect of the reaction between soils and toxic elements.

Medium to fine textured soil with pH >6.5 and 3% to 7% organic matter are best for application of sludges high in potentially toxic elements.

The organic matter of soil is, weight for weight, more significant to toxic element retention than inorganic matter, yet our specific knowledge of the role and fate of organic matter in soils is most inadequate (Leeper, 1972). Unamended fields of mineral soils which are considered acceptable for toxic element loadings by the state of Wisconsin application guidelines range from 5 tons organic matter per acre (0.5%) to over 70 tons

per acre (7%) (Keeney, et al., 1975). Evidence cited by Leeper indicates that the power of organic matter to retain toxic elements is about the same as for inorganic matter (approximately 2% of C.E.C.), but organic matter tends to have a much higher C.E.C. value. This relation is readily observed when comparing "pure" humus and "pure" clay as illustrated in Figure 6 (Brady, 1974). Unfortunately, organic matter decays at rates somewhat dependent on climate, and the protective effect of organic matter then is lost (Chaney, 1973; Mann and Barnes, 1957). A method for calculating organic matter accumulation and decay in soil is given by Leeper (1972). The effect of organic matter accumulation from sludge amendments is expected to be slight, and the factors accounting for this are discussed in Module 17, "Organic Matter".

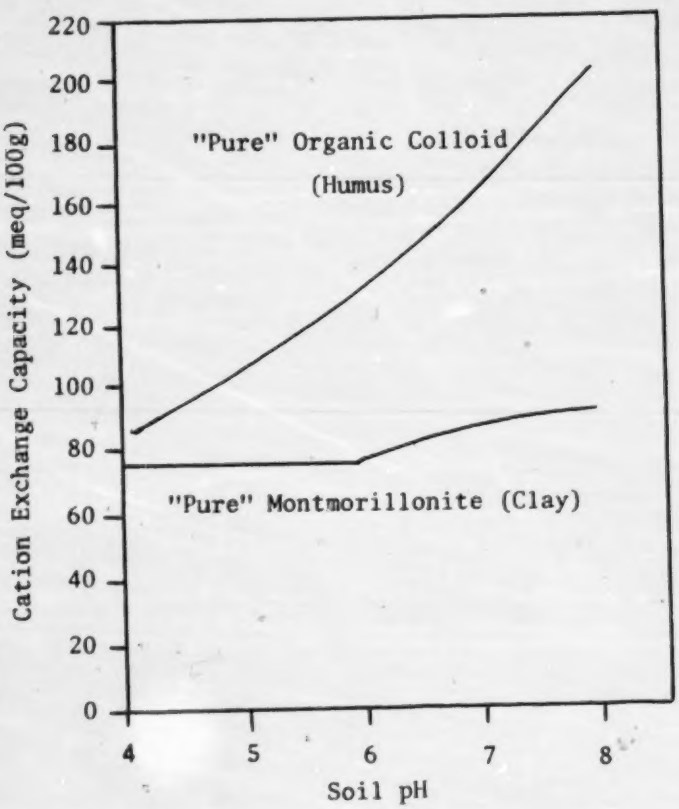

Figure 6

The cation exchange capacity of organic colloids increases with pH more rapidly than that of inorganic colloids (adapted from Brady, 1974).

Sludge Loading Rates

There are various opinions as to what sludge loading constitutes an acceptable rate. Several such viewpoints are summarized in Table 4.

Table 4. Sludge loadings vary widely, yet all have been reported as causing "no significant effect" on vegetation (adapted from Kirkham, 1974).

Authority	Recommended Load Rate
National Swedish Board of Health and Welfare (Emmelin, 1973)	0.43 short ton/acre-yr
Hinesly (1972)	27 short tons/acre-yr (5 yr average)
Metropolitan Sanitary District of Greater Chicago (Lyman, et al., 1972)	"similar to Hinesly"
Le Riche (1968) (England)	29 short tons/acre-yr (19 yr average)

Zinc Equivalent (Z.E.)

Chumbley (1971) gathered a considerable body of experience with potentially toxic elements through his research in England. To arrive at a usable, broad generality, Chumbley neglected any toxic effects due to elements other than zinc (Zn), nickel (Ni), and Copper (Cu) (Chaney, 1973; 1974). He then defined "Zinc Equivalent" (Z.E.) as a coefficient expressing a concentration of toxicants, weighted in terms of zinc (assuming copper and nickel to be two times and 8 times more toxic than zinc respectively). Thus:

The major concept which has been used for toxic element calculations over the past several years is Zinc Equivalent.

1) $Z.E.\ ug/g = Zn^{+2}\ ug/g + 2(Cu^{+2}\ ug/g) + 8(Ni^{+2} ug/g)$

For example, if a sludge was found to have the

maximum levels of toxic elements (dry weight basis) recommended by Chaney (1974) it would contain:

Zn = 2000 ug/g
Cu = 1000 ug/g
Ni = 200 ug/g
Cd = 1% of Zn
Pb = 1000 ug/g
Hg = 10 ug/g
Cr = 1000 ug/g

The zinc equivalent of that contaminated sludge would be:

Z.E. ug/g = 2000 ug/g + 2(1000 ug/g) + 8(200 ug/g)
Z.E. = 5600 ug/g

Cation Exchange Capacity (C.E.C.)

The Cation Exchange Capacity (C.E.C.) of soils is a parameter readily evaluated by soil chemists and used as an index of toxic element retention (Chaney, 1974; Page, 1974; Leeper, 1972; Chumbley, 1971; Allaway, 1977).

Soil C.E.C. is the best ordinarily measured characteristic of soils which relates to the ability of soils to hold excess toxic elements.

It must not be thought that significant toxic element retention necessarily occurs on the exchange site measured by the C.E.C. analyses. Rather, C.E.C. values only give the net effect of all negatively charged surfaces, whether crystalline or amorphous (Leeper, 1972). Toxic element concentrations are always too low to compete extensively with normal soil Na^{+1} and Ca^{+2} ions. Nevertheless, soil C.E.C. is the best ordinarily measured character of soils which relates to the ability of a soil to hold excess toxic element (Chaney, 1974). It has been the practice of various researchers to assume a maximum loading of potentially toxic elements equal to some percentage of the soil C.E.C. As a general rule, Leeper (1972) recommends that the total toxic element load which could be added safely to unamended soils should not exceed 5.0% of the soil C.E.C. at pH greater than 6.5. This is similar to Chaney's (1973) conclusion and the recommendation of the British Ministry of Agriculture, Foods and Fisheries

reviewed by Chumbley (1971). Chaney (1974) makes a very strong effort to emphasize that Leeper's generality is decidely unsafe for general farming needs at pH values less than 6.5.

Before continuing, it would be informative to glance at C.E.C. values associated with various soils.

Table 5. C.E.C. values of surface soils of the United States having a large range (from Brady, 1974, p. 102).

Soil Type	C.E.C. (meq/100 g)
Sand	
Sassafras (N.J.)	2.0
Plainfield (Wisc.)	3.5
Sandy Loam	
Greenville (Ala.)	2.3
Cecil (S.C.)	5.5
Colma (Calif.)	17.1
Loam	
Sassafras (N.J.)	7.5
Dover (N.J.)	14.0
Silt Loam	
Delta (Miss.)	9.4
Dawes (Nebr.)	18.4
Grundy (Ill.)	26.3
Clay and Clay Loam	
Cecil clay loam (Ala.)	4.0
Coyuco sandy clay (Calif.)	20.2
Sweeney clay (Calif.)	57.2

The range of C.E.C. values is significant. Clearly sandy soils have very low values whereas some organic soils may have C.E.C. values extending from 250-400 meq/100 g (Leeper, 1972).

The U.S. Department of Agriculture has developed guidelines for cumulative metals addition in sludge to cropland based on soil CEC (Table 6). These guidelines also form part of the recommendations for toxic element additions issued by the EPA (Jorling, 1977). Table 6 relates to privately owned farmland. EPA suggests that higher application rates may be acceptable on publicly-owned farmland or land dedicated to waste disposal, where adequate monitoring safeguards are employed.

Table 6. Maximum Sludge Metal Addition to Farmland (Over the Site Lifetime)

	Maximum Metal Addition (kg/ha) to Soil with a C.E.C. (meq/100 g) of:		
Metal	Less than 5	5-15	Greater than 15
Pb	500	1000	2000
Zn	250	500	1000
Cu	125	250	500
Ni	50	100	200
Cd	5	10	20

These recommendations are reported in Dowdy, et al. (1976), who recommend three other safeguards to be used concurrently: a) initial soil pH of 6.5 (determined on samples of 1:1 soil/water ratio) or greater, and maintained at 6.2 or greater when application begins; b) leafy vegetables not to be grown; c) Cd additions not to exceed 2 kg/ha-year (this is very conservative).

Table 6 represents an attempt to limit application rationally on the basis of the most important soil property for metal ions, C.E.C. As is noted in CAST (1976), the zinc equivalent theory was based on limited data, although the best available at the time, and new information shows that toxicities of Zn, Ni, and Cu are not necessarily additive. The ZE concept is felt to underestimate greatly the amounts of metals which can be applied to soils of near-neutral to higher pH. ZE also does not apply to a broad range of plants.

The ZE theory is presented here as a method of determining applications which has been used extensively over the past several years and may continue to find use in some quarters. The USDA guidelines are presented as illustrative of the trend at present and as a method which may be used extensively in the near future. Both concepts should be familiar to the designer of sludge application sites.

Present State of Sludge Guidelines

The differences between the ZE and USDA recommendations are further illustrated by the following discussion involving ZE and two other more recent and widely used methods of quantifying sludge application rates based on metal additions. The entire field of sludge limiting parameters is just developing and is in a state of flux. Other guidelines, such as those being developed at Penn State University, are being proposed. The designer will have to remain closely attuned to the current literature for guidance.

New guidelines for determining sludge application rates are being developed at a rapid rate. The designer is urged to keep abreast of this information.

The remaining part of this module presents sample computations of sludge application rates using different guidelines, and examining different possible limiting parameters. Potentially toxic element limits are compared to nitrogen and cadmium limits to determine an overall limiting factor for land application of a given sludge.

The equations which will be used to illustrate these points are those of Chaney, Chumbley (ZE), and the State of Wisconsin.

Other theories have been put forward which have attempted to incorporate soil C.E.C. This has resulted in other sludge application formulas which have been used as follows.

Soil CEC has been used in several sludge application guidelines.

Leeper suggested assigning a rough value of 15 meq/100g to the C.E.C. of "surface soils".

Chumbley chose to center attention on Leeper's 15 meq/100g, and calculated the amount of zinc needed to equal 5% of 15 meq/100g as follows:

GIVEN: A soil of C.E.C. = 15 meq/100g

FIND: Concentration of Zn^{+2} = 5% soil C.E.C.

METHOD: Atomic weight Zn = 66

eq. wt. Zn^{+2} = at. wt. ÷ 2 = 33 g Zn^{+2}

meq. wt. Zn^{+2} = 10^{-3} x eq. wt. = 0.033 g Zn^{+2}

15 meq. wt. Zn^{+2} = 15 x 0.033 g = 0.495 g Zn^{+2}

5% of 15 meq. wt. Zn^{+2} = 0.05 x 0.495 g = 0.025 g Zn^{+2}

Therefore:

5% soil C.E.C. (in Zn^{+2}) = 0.025 g Zn^{+2}/100 g soil

= <u>250 ug/g or 250 ppm Zn^{+2}</u>

The conclusion reached and widely reported is that unamended soils can be loaded up to 250 ppm with zinc with no particular danger.

A value which is more useful comes from determining the number of pounds per acre of zinc represented by, say, 250 ug Zn^{+2}/g soil. The calculation goes as follows:

LET: 1 acre - 6" = 2 x 10^6 lbs and 454 g = 1 lb

THEN: $$\frac{250 \text{ ug } Zn^{+2}}{\text{g soil}} \times \frac{\text{g}}{10^6 \text{ ug}} \times \frac{2 \times 10^6 \text{ lbs}}{\text{acre-6"}} = \frac{500 \text{ lbs } Zn^{+2}}{\text{acre-6" soil}}$$

AND $$\frac{500 \text{ lbs } Zn^{+2}}{\text{acre-6" soil}} \times \frac{454 \text{ kg}}{10^3 \text{ lb}} \times \frac{2.47 \text{ acres}}{\text{ha}} = \frac{561 \text{ kg } Zn^{+2}}{\text{ha soil}}$$

<u>Application Rate of Dry Sludge to Unamended Soils</u>

Assuming that a given soil has a C.E.C. of about 15 meq/100 g (so that it would be advisable to avoid loading more than 500 lbs Z.E./acre on unamended soil at pH > 6.5), how can that be translated to an application rate of an actual sludge?

Application rates (total lifetime load or annual loads) are calculated differently by three separate equations in common use: Chumbley, Chaney and Wisconsin Guidelines.

Three approaches are presented which are not mutually consistent. Each will be reviewed:

<u>Chaney's (1974) approach</u>: Chaney proposed that the annual application rate be calculated from a predetermined total application. His basic equation for determining the total site application for unamended soils of pH > 6.5 is:

2) Total sludge (dry tons/acre) $= \frac{16{,}300 \times \text{CEC}}{\text{Zinc Equivalent of sludge} - 300}$

(the -300 adjusts for the addition to the soil of some exchange capacity in the sludge matter).

Thus, for a soil of CEC = 15 and sludge ZE = 1400,

Total sludge (dry tons/acre) = 222 tons/acre.

For a 30 year span, that is about 7.4 tons per acre year or about 30 tons/acre for a single application once every four years.

Chaney: 30 tons/acre once every 4 years under given conditions. (CEC = 15; ZE = 1400)

Chumbley's (1971) approach: Chumbley chose to utilize a chart, reproduced as Table 7, to approach this problem. He illustrated its use by assuming that a sludge batch had a zinc equivalent of 1,400 mg/kg in the dry matter. From Table 5, that sludge could be applied safely to unamended soil at pH > 6.5 over a 30 year lifespan at a rate of one 22.4 tons/acre dry matter application once every four years.

Table 7. The tons of dry sludge per acre safely applied in a single application to unamended soil of pH > 6.5 depends on the number of years between applications and the zinc equivalence of the sludge (adapted from Chumbley, 1971).

Proposed number of years between single applications	Proposed rate of application (in tons/acre dry matter)[1] for sludge of given Z.E. assuming a 30 year site lifespan.					
	5.6	11.2	22.4	33.6	44.8	56.0
1	1510	750	370	250	190	150
2	3020	1510	750	500	380	300
3	4530	2260	1110	750	570	450
4	6040	3020	1510	1010	750	600
5	7550	3770	1880	1260	940	750

[1]It is assumed that Chumbley's values were in the customary English weight unit, the long ton, so the values of this table have been converted to the U.S. short ton (long ton x 1.12 = short ton).

Chumbley: 22.4 tons/acre once every four years under given conditions. (CEC = 15; ZE = 1400)

Wisconsin's approach: Wisconsin has adopted guidelines for sludge application based on an interim guide recommended by the EPA. It is similar to Chaney's approach, but is more liberal. The total sludge loading is calculated from the formula:

$$3)\quad \text{Total Sludge (dry tons/acre)} = \frac{32{,}500 \times \text{C.E.C.}}{Zn^{+2}\ \text{ug/g} + 2(Cu^{+2}\ \text{ug/g}) + 4(Ni^{+2}\ \text{ug/g})}$$

Notice these features of that formula:

1) Toxic element additions are limited to 10% of soil C.E.C. instead of Chaney's recommended 5%.

If a soil analysis identifies the load of available toxic element to be, say, 100 ug/g Zn^{+2}, 40 ug/g Cu^{+2}, and 2.5 ug/g Ni^{+2} (viz. Z.E. = 160), and if the soil is a silt loam of 3.2% organic matter Table 7 could be used as follows:

An acre-furrow slice (6 in) of soil weighs roughly 2×10^6 lbs, therefore, the soil in question contains $(2 \times 10^6 \times .032)/2000 = 32$ tons organic matter/acre. A silt loam of that organic matter content is permitted to have a loading of 1110 metal equivalents. The metal equivalents of available toxic element of this soil is

$$\text{metal equivalents} = \frac{100 + 2(40) + 4(2.5)}{500} = 0.38$$

Therefore, this soil could be permitted to receive 1110-0.38 = 1109.62 metal equivalents over its life-span. For all practical uses this is, of course, 1110 metal equivalents.

If the sludge is the same sludge previously used in this module as an example, (1020 ug/g Zn^{+2}, 150 ug/g Cu^{+2}, and 10 ug/g Ni^{+2}) it contains

$$\text{metal equivalents} = \frac{1020 + 2(150) + 4(10)}{500}$$

$$= 2.72 \text{ lbs/ton sludge}$$

therefore, a total of

(1109.62 lbs/2.72 lbs) x tons sludge = 408 tons sludge.

The site thus can receive (408/30) x 4 = 54 tons sludge once every fourth year for 30 years.

Wisconsin: 54 tons/ acre every four years under given conditions. (CEC = 15; ZE = 1400)

A comparison of these three guidelines (Chumbley, Chaney, and Wisconsin) in sludge application rates to previously amended soils (which have already received sludge application) shows that the approaches differ much more widely in permissible loadings to previously amended than to unamended soils.

Nitrogen Versus Potentially Toxic Element Loading:

Using sludges for fertilizers raises questions about the limiting factors inherent in N, potentially toxic elements, and Cd loads of sludges.

The application of sludge to land often is recommended. Some see it as a simple matter of recycling natural products. Others may cite benefits in increased soil aggregation (Epstein, 1973; Lunt, 1953) and soil condition (Olds, 1960) while many see sludge as a cheap fertilizer. Chaney (1974) notes that if the toxic element concentration of sludge does not exceed his recommended values for "domestic" sewage, and if soil pH is maintained at pH > 6.5, trace element fertilizer values will be realized for food crops. However, more commonly, much is made of the nitrogen fertilizer value of sludges (Kirkham, 1974).

The complex role of nitrogen of wastewaters and its interaction with soils is reviewed in Module 15, "Nitrogen Considerations". Nitrogen loadings are discussed and a rough estimate is made that agricultural soils may require 300 to 400 lbs nitrogen per acre for fertilization. The question suggested by this is whether toxic element loads or nitrogen loads act as limiting factors in application schedules. Similarly, it would be expected that there should be some maximum lifespan for sites and certain minimum values for soil C.E.C. that could be associated with a given sludge.

The equations used here for these determinations are equations (6) and (7), based on Chaney's recommendations and the Wisconsin guidelines, respectively. Other guidelines could also be used.

$$6)\ \frac{n\ lb}{acre\text{-}yr} = \frac{16{,}300 \times CEC}{Z.E. - 300}\ \frac{Tons}{acre} \times \frac{1}{L\ yr}\ \frac{2000\ lb}{Ton} \times \frac{\phi}{10^6}$$

$$7)\ \frac{n\ lb}{acre\text{-}yr} = \frac{32{,}500 \times CEC}{Z.E._{(w)}}\ \frac{Tons}{acre} \times \frac{1}{L\ yr} \times \frac{2000\ lb}{Ton} \times \frac{\phi}{10^6}$$

where, in each equation:

n = lbs N/acre-yr desired for optimum nitrogen fertilization

Z.E. = Zn^{+2} ug/g + 2(Cu^{+2} ug/g) + 8(Ni^{+2} ug/g)

$Z.E._{(w)}$ = Zn^{+2} ug/g + 2(Cu^{+2} ug/g) + 4(Ni^{+2} ug/g) (Wisconsin)

L = site lifespan in years

ϕ = maximum concentration of N (in mg/kg) in sludge which will give the desired N/acre-yr loading

C.E.C. = cation exchange (in meq/100 g)

To illustrate how these equations may be used to answer the questions stated earlier, use is made of the data from two anaerobically digested sludges of the Metropolitan District of Chicago as reported by Hinesly (1972). Their assay values are reproduced in part in Table 8.

Table 8. Concentrations of selected chemicals in Chicago sludges are given as reported by two treatment plants (adapted from Hinesly, 1972).[1]

	Stickney		Calumet	
	Given ppm	Calc.[1] mg/kg	Given ppm	Calc.[1] mg/kg
Cd	14	321	3.0	146
Zn	223	5,115	83.0	4,049
Cu	67	1,537	16.0	780
Ni	15	344	3.0	146
N	2,860[2]	65,596	2,150[3]	104,878
Z.E.		10,941		6,777
$Z.E._{(w)}$		9,565		6,193
Total Solids	43,600		20,500	

[1] Calc. mg/kg = ppm element x 10^6/ppm solids

[2] N = "Total-N" + "NH_4-N". These are 1560 ppm and (assumed) 1300 ppm respectively.

[3] N = "Total-N" + "NH_4-N". These are 1500 ppm and 650 ppm respectively.

Question 1: Will toxic elements or nitrogen be limiting in these sludges?

Method for determining limiting factors: Solve equations 6 and 7 for ϕ and rearrange to get:

8) $\phi_1 = Z.E.\ (m) - k$

9) $\phi_2 = Z.E._{(w)}\ (\gamma)$

where:

ϕ_1 = maximum concentration of N (in mg/kg) in sludge needed to achieve desired fertilizer value, based on Chaney's recommendation

ϕ_2 = same as ϕ_1 except based on Wisconsin's recommendations

Z.E. and $Z.E._{(w)}$ assume values previously defined

$m = \frac{nL}{32.6 \times C.E.C.}$

$\gamma = \frac{nL}{65 \times C.E.C.}$ where n, L, and C.E.C. have values as defined earlier

$k = 300\ (m)$

On substitution of values, if Total N (σ) is considered to be Kjeldahl N of sludge, then if:

1. ϕ_1 or ϕ_2 > total N, toxic elements are limiting
2. ϕ_1 or ϕ_2 = total N, toxic elements and nitrogen are simultaneously limiting.
3. ϕ_1 or ϕ_2 < total N, nitrogen is limiting.

Example:

Assume C.E.C. = 15 meq/100 g
L = 30 years
Z.E. = 10,941 ug/g (Stickney sludge, Table 8)
$Z.E._{(w)}$ = 9565 ug/g
n = 400 lbs N/acre-yr
σ = Total N = 65,596 mg/kg

$$\phi_1 = 10941 \frac{ug}{g} \times \frac{400\ lbs}{acre\text{-}yr} \times 30\ yr \times \frac{1}{32.6 \times 15} = 268{,}491\ mg/kg$$

ϕ_1 > Total N, therefore, for given conditions, toxic element is limiting based on Chaney's recommendations.

$$\phi_2 = 9565 \frac{ug}{g} \times \frac{400\ lbs}{acre\text{-}yr} \times 30\ yr \times \frac{1}{65 \times 15} = 117{,}723\ mg/kg$$

ϕ_2 > Total N, therefore, for given conditions, toxic element is limiting based on the Wisconsin guidelines.

Effective Lifespan:

Method for determining the effective lifespan of a site: Substitute σ for ϕ in equations 6 and 7 and solve for L (lifespan).

10) $$L_1 = \frac{32.6 \times CEC \times \sigma}{n(Z.E. - 300)}$$

$$L_2 = \frac{65 \times CEC \times \sigma}{n(Z.E._w)}$$

where:

L_1 = lifetime based on Chaney's recommendation
L_2 = lifetime based on Wisconsin guidelines
σ = total N of sludge, dry wt. (Kjeldahl-N+NH_4-N)
C.E.C., n, Z.E. and $Z.E._{(w)}$ values remain as

Question 2: What is the maximum length of time that a given site can be used until its toxic element limit is reached assuming sludge loading rates are held at levels deemed optimal for N fertilization?

defined earlier.

Example:

σ = 65,596 mg/kg (Stickney Sludge, Table 8)

C.E.C. = 15 meq/100 g

n = 400 lbs N/acre-year

Z.E. = 10,941 ug/g

$Z.E._{(w)}$ = 9,565 ug/g

$$L_1 = \frac{32.6 \times 15 \times 65,596}{400\ (10,941 - 300)} = 7.54 \text{ years}$$

$$L_2 = \frac{65 \times 15 \times 65,596}{400\ (9,565)} = 16.72 \text{ years}$$

C.E.C. Value Computed:

Method for determining the C.E.C. value needed in a soil: Solve equations 6 and 7 for C.E.C. and substitute σ for ϕ as described earlier:

Question 3: What soil C.E.C. value would be needed to assure a desired lifespan for a given sludge being applied at an optimal N fertilizing rate?

(12) $$C.E.C._1 = \frac{nL(Z.E. - 300)}{32.6 \times \sigma}$$

(13) $$C.E.C._2 = \frac{nL(Z.E._{(w)})}{65.5 \times \sigma}$$

where $C.E.C._1$ and $C.E.C._2$ are values based on the recommendations of Chaney and Wisconsin respectively.

n, L, Z.E., $Z.E._{(w)}$ and σ remain as defined earlier.

Example: σ = 65,596 mg/kg

n = 400 lbs N/acre-yr

Z.E. = 10,941

$Z.E._{(w)}$ = 9,565

L = 20 years

$$C.E.C._1 = \frac{400 \times 20 \times (10,941 - 300)}{32.6 \times 65,596} = 39.8 \text{ meq/100 g}$$

$$C.E.C._2 = \frac{400 \times 20 \times 9,565}{65 \times 65,546} = 17.9 \text{ meq/100 g}$$

Confusion caused by the use of "ppm" may cause serious problems. This is particularly true when looking at data expressing nitrogen concentrations. Care must be taken to be assured that:

Question 4: What is meant by "ppm N"?

1. "Nitrogen" values are expressed in dry weight values (mg/kg) before substituting into the above equations.
2. "Total N" is the sum of organic N and NH_4^+-N (also Kjeldahl N alone is called "total N".)

Cadmium Loading Rate:

Chaney (1974) recommends that no sludges be added to soils in which the cadmium concentration exceeds 1.0% of the zinc.

Cadmium is a serious limiting parameter because of the possibility of harmful health effects. Guidelines differ on the method of calculating acceptable Cd loadings.

The Wisconsin guidelines are far more conservative in this respect. There, cadmium additions must not exceed 2 lbs per acre per year and the total site lifetime maximum of 20 lbs per acre (Keeney, et al., 1975).

To illustrate these guidelines, reconsider Hinesly's (1972) data (Table 8). Based on Chaney's recommendations, the Stickney sludge contains cadmium at a level of 6.3% zinc while the Calumet sludge contains cadmium at a level of 3.6% zinc. Clearly, neither sludge is suitable for land application according to Chaney.

The Wisconsin guidelines would not exclude the use of these sludges on soils. However, the application rate would have to be calculated in terms of cadmium limitations. The method recommended is as follows:

14) ANNUAL load limit due to Cd = 2 x 500/Cd mg/kg = 3.1 tons (Stickney) and 6.8 tons (Calumet) sludge per acre per year. The total LIFESPAN cadmium load, however, must not exceed 20 lbs/acre according to the Wisconsin guidelines. That amounts to 31 tons (Stickney) and 68 tons (Calumet) sludge per acre. To determine whether Cd is limiting, is necessary to evaluate both ANNUAL and LIFESPAN parameters.

This amounts to a simple comparison between these permissible cadmium loadings and loadings set by zinc

equivalent values or nitrogen. Previous calculations in this module have shown that Chaney's recommendations would allow a lifetime loading (30 years, C.E.C. = 15 meq/yr, pH > 6.5, unamended soil) of 23 and 38 tons/acre for Stickney and Calumet sludges respectively. These become 0.77 and 1.26 tons/acre-yr. Clearly toxic element loading is limiting with respect to cadmium on an annual basis.

In these cases, it is apparent that toxic element also is limiting with respect to lifetime loading and with respect to nitrogen ($\phi > \sigma$ in each case).

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